NASA-CR-203795

7N-26-CR
032530

Channel Segregation in Alloy Ingots

A. Hellawell
Department of Metallurgical Engineering
Michigan Technological University
Houghton, MI

ABSTRACT

General patterns of fluid flow are considered for various geometrical arrangements with interdendritic liquid either less or more dense than bulk liquid. The incidence of channel formation is described and mechanisms disucssed for channel nucleation, propogation and prevention. It is concluded that channels form by perturbation of the bulk liquid from regions close to the dendritic growth front and the relevance of this model is discussed.

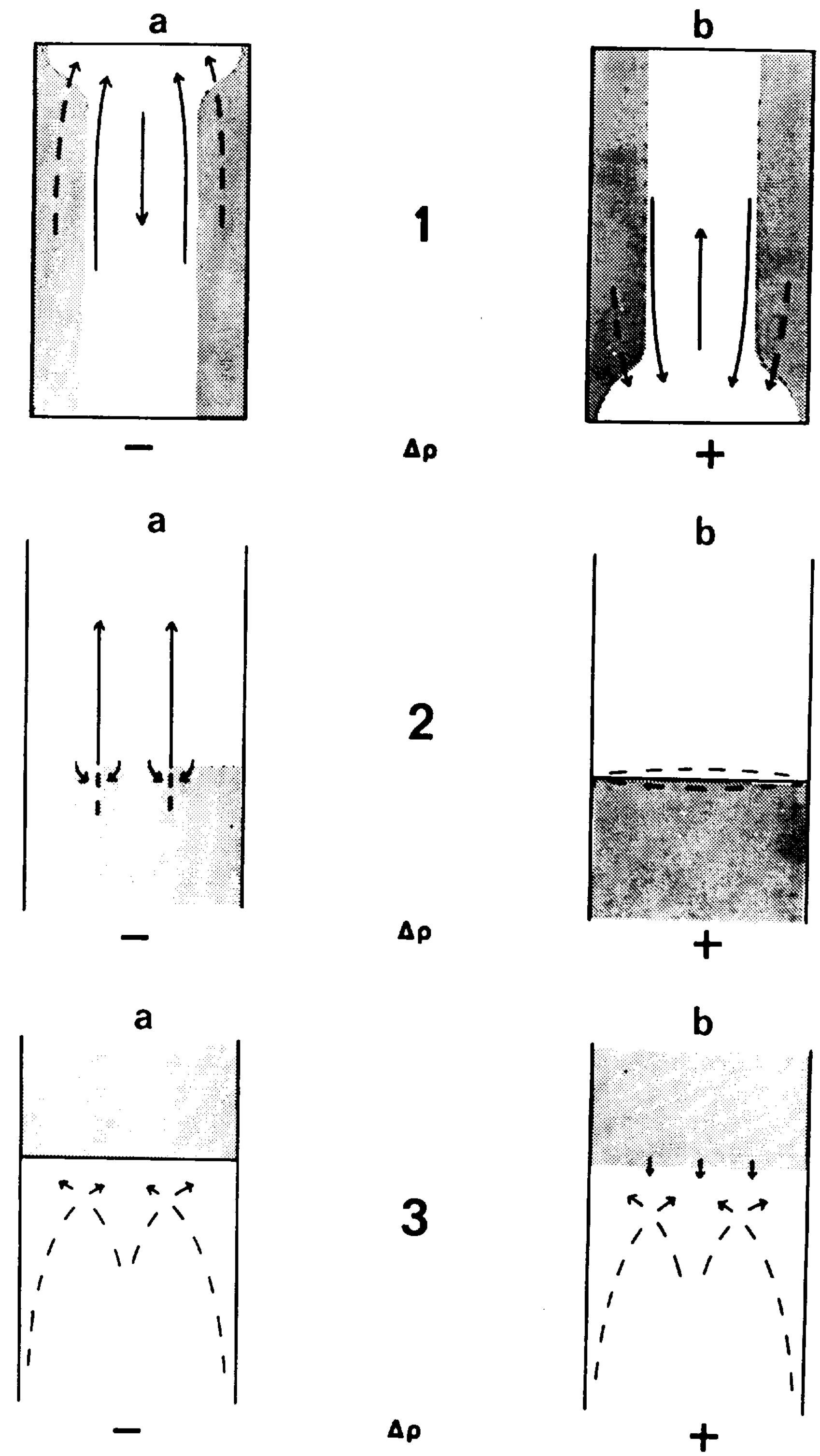
INTRODUCTION

During solidification of alloys in which there is a significant freezing range, coring or interdendritic micro-segregation occurs, as is well known. While partly solidified the interdendritic liquid composition and temperature invariably differ from those of the original melt or remaining bulk of liquid and therefore density gradients are common which provide driving forces for convection. Density variations with temperature d__/dT depend on the liquid coefficients of thermal expansion which are small and in general, if the component densities are unequal the compositional dependence, d_/dC, predominates and can obviously be positive or negative. Our concern then, is with density variations down a liquidus line or surface, along or across which the compositional dependence may either reinforce or counteract thermal density dependence. The consequences of such density gradients are illustrated by macroscopic segregation and have been treated in a general way to arrive at expected interdendritic flow patterns involving flow compelled by contractions during freezing, gravitational and centripetal forces [1,2].

In addition to general macroscopic flow patterns within the mushy zone of a casting there can also develop localized segregation channels which run approximately vertically, are 0.1 m to 1 m long and as much as an order of magnitude wider than the average interdendritic spacings. These channels typically appear at longer times, > 10^3 s, so that they are found in larger castings or in slowly solidified ingots. In steel billet castings such channels are termed "A" segregates or in directionally solidified specimens, such as E.S.R. ingots, they are known as "freckles". In specialized applications the presence or absence of such defects can make the difference between rejection or acceptance of a cast product.

GEOMETRICAL ALTERNATIVES

The examples mentioned are associated with alloys in which the density-composition dependence exceeds that due to temperature gradients and the solute(s) is less dense than the solvent, e.g. carbon, sulphur, phosphorus in steels, but clearly there are various combinations of density gradient and growth direction. Possible extremes of heat flow direction and density - temperature - composition dependencies can be summarized as in Figure 1-3. Heat flow directions may be identified as being horizontal (billet castings), vertically downwards parallel to gravity, i.e. growth upwards antiparallel to gravity (E.S.R. ingots) or vertically upwards antiparallel to gravity, i.e. growth downwards. These geometrical



Figures 1., 2., 3.

alternatives are then combined with density dependencies: d_/dt is always negative and d_/dC may be of either sign, as already noted. The resulting patterns of convective flow are rather different in each case and depend on both the interdendritic vs. bulk liquid relative densities and on the local gradients arising from solute rejection at the dendritic growth front. The alternatives are as follows:

Figure 1, horizontal growth; (a), with less dense solute such that d_/dC < d_/dT (i.e. more negative and domi-nant), causes a general convective pattern in the bulk liquid, upwards at the growth front, downwards in the center and with a buoyancy of inter-dendritic liquid relative to that of the bulk; (b), the reverse density depen-dence, with more dense solute flowing downwards at the front and sinking through the mushy zone with concommitent upward flow in the center.

These cases have been widely examined: case 1(a) is examplified by medium to high carbon steel (plus sulphur, phos-phorus, etc.) [10], while case 1(b) has been studies in Cu-Pb [8] and Al-Cu alloys [18]. Both cases have been examined using transparent models with aqueous salt solutions of ammonium chloride and with ternary additions of zinc chloride [3-7]. Crystallization of NH_4Cl involves rejection of water as a solute and a decreased liquid density; with more dense $ZnCl_2$ present the rejected liquid becomes more dense at a concentration of about 6-8 wt.% [9].

Figure 2 with vertical growth upwards, if the solute is less dense, (a), a situation arises where the interdendri-tic liquid is less dense than the bulk, which is, however, stabilized against convection by a positive temperature gradient. This density inversion can only be accommodated by localized convection upwards which must be suppli-ed by simultaneous downward entrainment; there are therefore no overall fluid flow pattern such as those of Figure 1. If the solute is more dense, (b), and the upward temperature gradient is positive, the fluid is doubly stabilized against convection and macroscopic redistribution of solute can only occur if the growth front develops macroscopic curvature (which it often does).

Both these combinations have been studied in metallic and aqueous systems and in some ways this arrangement is the simplest of the alternatives. Using the transparent model system, NH_4Cl-H_2O, it has been shown [3-7] that the local upward flow, Figure 2(a), result from liquid rising out of channels which run back into the mushy zone and that a plume of less dense liquid rises out of each channel towards the the upper surface of the bullk liquid, Figure 4. Such channels develop after an incubation time of some 10-15 minutes and are fairly evenly spaced, Figure 5; these are the "freckles" mentioned earlier and they run vertically, even if the mold is tilted [5].

The quiescent situation of Figure 2(b) is, in practice, very difficult to maintain because the growth front isotherm is easily distorted. Thus, with even a slight lateral component of heat flow, the front becomes concave upwards and as the more dense solute collects in the middle of the casting a depressed sump develops, a situation well known in aluminum DC ingots. In narrow samples e. g. 5 mm diameter, such as in laboratory scale directional growth experiments, the reverse tendency leads to a front which is increasingly convex upwards and macrosegregation then develops laterally. In neither case (concave up/downward) do localized channels occur, nor would they be expected. However, referring to Figure 2(a) where channels do develop, if the growth front is distorted the channels are concentrated in the uppermost regions of the front, i.e. center or edges.

Figure 3 is a geometrical arrangement which is not commonly encountered in metallurgical contexts but is very familar to crystal growers using the Czochralski technique; the patterns of flow are again different from the cases of Figures 1 or 2. With solute less dense, 3(a), the liquid adjacent to the front is stabilized against convection, but at a lower level, with a positive temperature gradient downwards, there will be temperature inversion in the bulk liquid; longer range convective flows are then to be expected, either up the center and down the sides or vice versa. In figure 3(b) the arrangement might be expected to be analogous to that of 2(a) but the bulk liquid is not stabilized against convection and the longer range thermal patterns would be expected to disturb any local entrainment pattern which might attend channel formation. These cases have not received attention in the context of channel formation.

While the general flow tendencies of Figures 1-3 can easily be recognized there are several features pertaining to channel development which need clarification; these are (i), by what mechanism(s) do the channels actually originate, (ii), what controls their dimensions and spatial distributions and (iii), other than selecting particular combinations such as those of Figures 2(b), 3(a) or possibly 3(b), what else might be done to inhibit channel formation? To answer these questions, the base chill configuration of Figure 2(a) has been selected as one being the most convenient for experiment, interpretation and analysis. Extension to the other arrangements is discussed subsequently.

METAL-ANALOGUE SYSTEMS

Experiments with transparent aqueous salt solutions, notably with NH_4Cl-H_2O, provide invaluable direct qualitative or semi quantitative evidence of various factors and mechanisms. They are, however, limited in that within the temperature range available (i.e. $< 100^{\circ}C$) only small compositional ranges can be studied, in these the fraction of solid in the mushy zone is also small, e.g. _ 10 by volume, and the dendritic mesh is therefore very open or permeable by comparison with that which may be found in metallic alloys, Figure 6. The other important difference between the aqueous and metallic systems is in the thermal conductivities which differ by some five order of magnitude.

In what follows here reference will be made to experimental studies with the above mentioned aqueous system and with lead rich alloys in the Pb-Sn system, where tin is the less dense component; both therefore correspond to Figure 2(a).

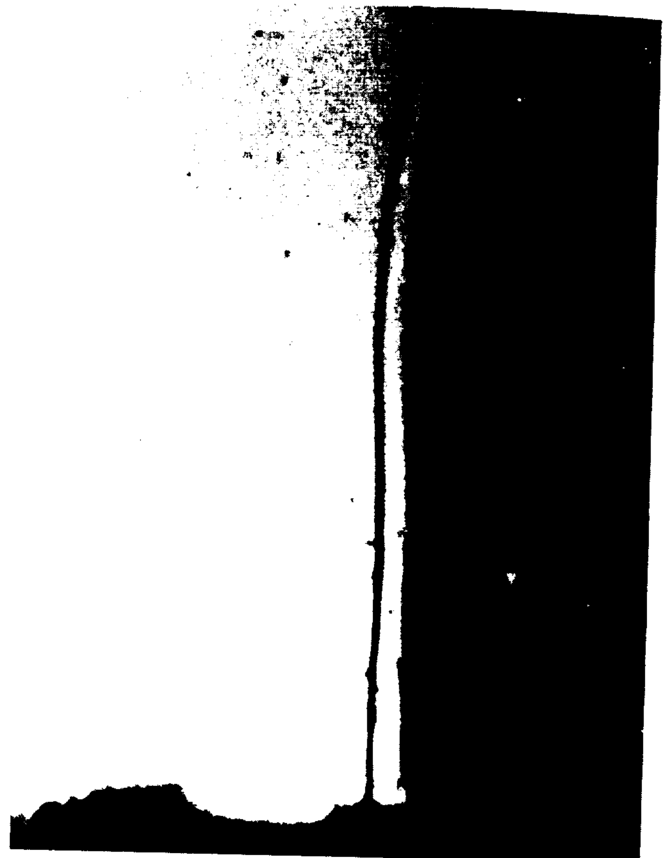


Figure 4.

CHANNEL NUCLEATION

With a perfectly uniform dendritic array and essentially horizontal isotherms the probability of channel nucleation should be equal in all parts of the system - somewhat analogous to homogeneous nucleation.

It is observed that channels do not form until growth has taken place for some time and distance, generally when the growth rate has fallen from that after the initial chill to a relatively constant value; in the analogue experiments to between 10 _m s-1 and 20 _m s-1. There is therfore an incubation time for whatever type of perturbation is necessary which may correspond to adjustment to some necessary conditions of growth rate, temperature and/or solute profiles [5,9], or to some dimensional condition within the mushy zone such as might attend ripening of the array behind the growth front. Further, it is also known that as soon as a channel develops there is a concommitent plume of less dense liquid

Figure 5.

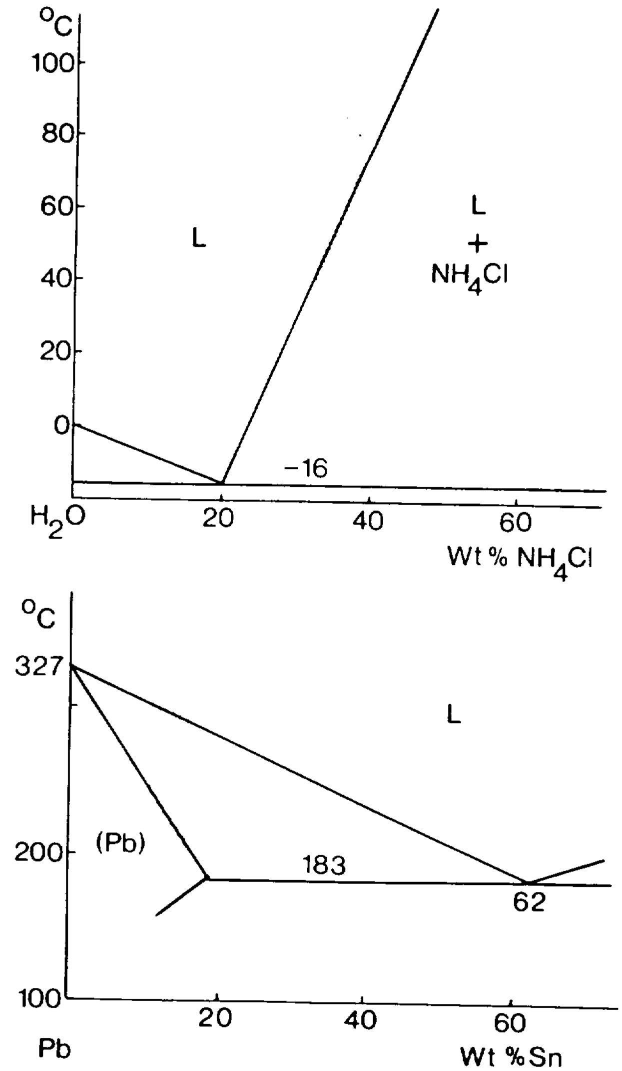


Figure 6.

issuing from the mouth of the channel, extending far into the bulk liquid, nearly to the upper surface, Figure 4. The fluid flow is therefore continuous from below to above the level of the growth front.

One assumption has been that the channels originate within the dendrite array [17,18] as by some internal perturbation at a growth imperfection. An objection to this idea would be that local acceleration of fluid flow is not possible without equivalent flows everywhere else in the mushy zone. The situation, with a positive temperatue gradient is of a less dense entrapped liquid, surmounted by a body of more dense liquid which is thermally stabilizied against convection (i.e. warmer at the top). The analogy has been drawn [6] with a body of stagnant liquid in a swamp which can be released only by a breach at the side and not by producing an internal trench, i.e. a channel must originate at, or very close to the dendritic growth front. This has been demonstrated with transparent materials in several ways [7]:

(a) Direct observation of channels which form at the sides of the mold show that the initial event begins at the growth front and is followed by rapid extension of the channel backwards into the dendritic mesh, Figure 7 (a-c),

(b) Artificially created channels, made by boring fine holes into the mushy zone fail to develop and those temporarily blocked fail to propogate, Figure 8 (a), while-

(c) Artifically created plumes formed by sucking up liquid ahead of the growth front do result in channel formation below those positions, Figure 8 (b).

Therefore, in this base chill configuration, certainly, and in other arrangements, probably, the formation of channels requires bulk liquid perturbation close to the growth front, Figure 9 illustrates a probable sequence in their formation.

CHANNEL GROWTH

It is observed that channels run vertically, and in tilted molds, with the growth front inclined to the vertical by up to 30^0, channel patterns can be traced on successive sections, Figure 5, and similarly observed directly in transparent materials. As may be seen, channels are not necessarily uniform in spacing or closely packed in distribution, although if two are very close together one may discontinue or both may do so, subsequently being replaced by a new channel nearby. It seems probable that the distribution reflects that of almost randomly sited nucleation events; there does not seem to be any correlation with grain boundaries. However, once a certain overall density of channels has developed, each channel must be supplied by a local, downward entrainment volume, Figure 10, and the establishment of these probably precludes, further perturbations. Channels which are too close to each other must compete for liquid and therefore one generally 'dries up'. Ther resulting assembly is then approximately steady state and continues almost indefinitely as long as, or even after, the growth front ceases to advance and or the supernatant liquid is exhausted. Measurements of fluid flow rates in solute plumes and entrainment times which can be found using colored dye in transparent systems, are compatible with streamlined flow and with known density and viscosity data [7].

CHANNEL PREVENTION

Rather obviously, channels would not be expected without either density gradients or gravitational acceleration to cause convection. The first of these requirements can be demonstrated by adding a third component to a binary system and so adjusting the composition temperature-density variations to a minimum; this has been done in metallic systems [8] and in the NH_4Cl-H_2O system by addition of a denser salt $ZnCl_2$ [4]. Measurements of density variations with ternary composition and temperature, i.e. across the segregation

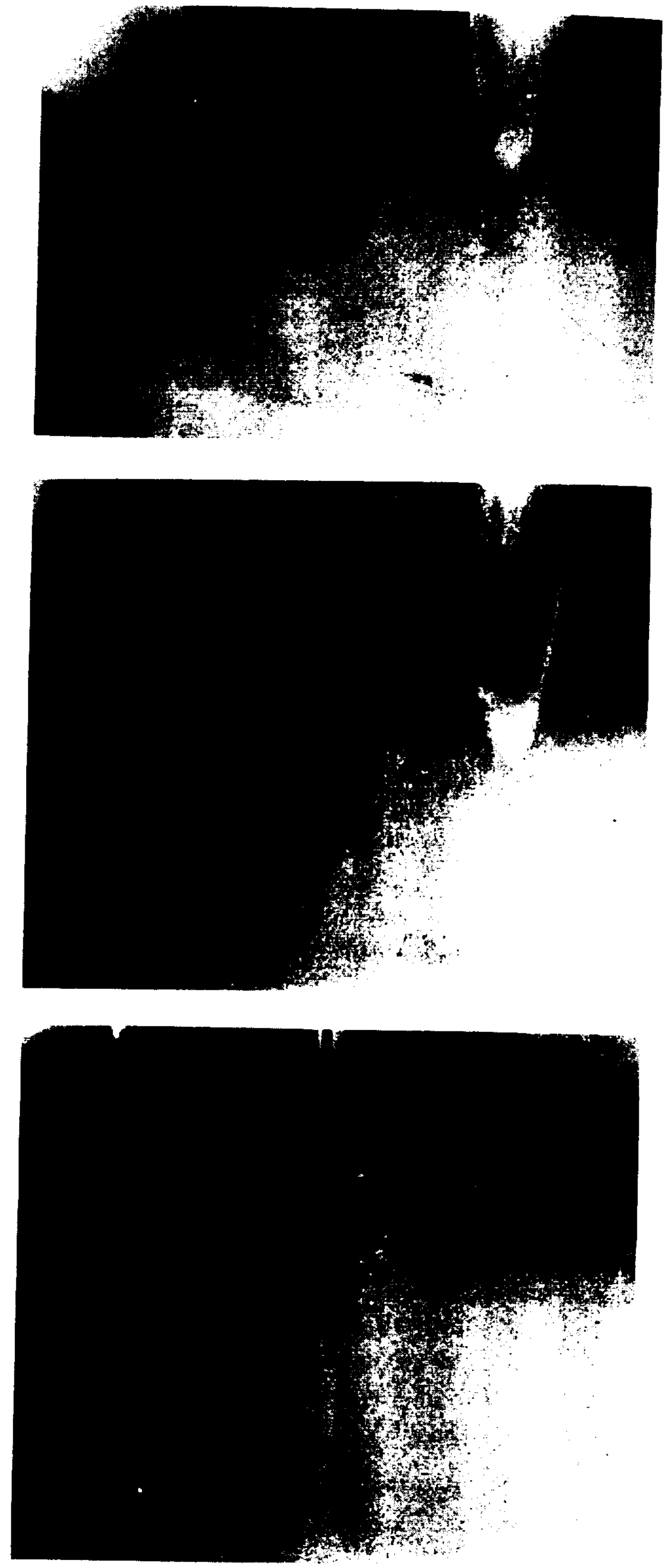


Figure 7.

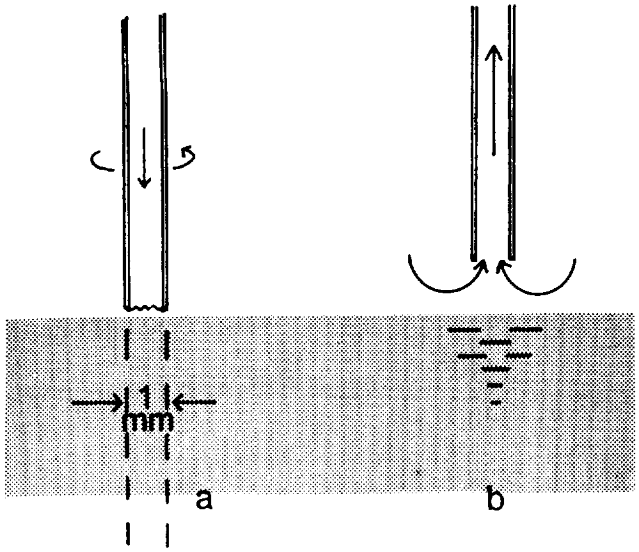


Figure 8.

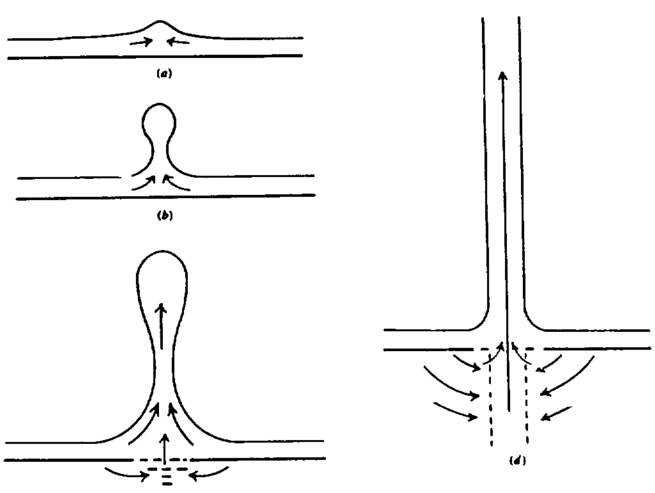


Figure 9.

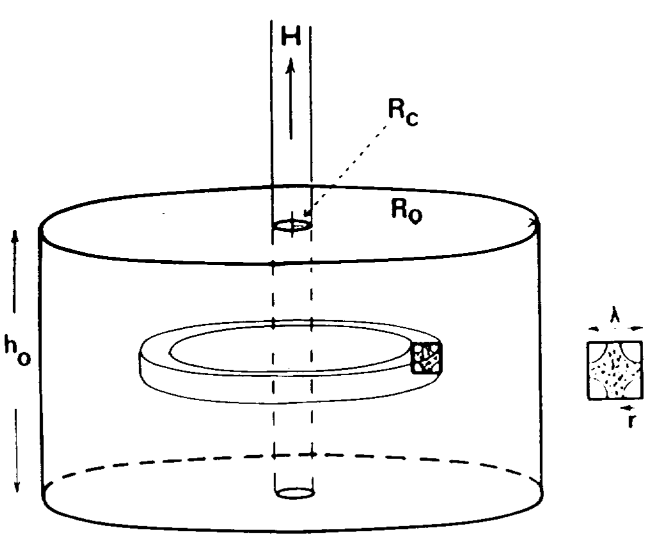


Figure 10.

trace on a ternary liquidus surface show [9] quite conclusively that the critical composition range for no channel formation is close to that where there are negligible density gradients. The other alternative, which would involve a low gravitational environment has yet to be demonstrated.

Less obviously, certain types of mold or liquid agitation can also inhibit channel formation, at least in the base chilled configuration. The movement which is effective is one of slow rotation (< 5 r.p.m.) about an axis inclinded to the vertical by up to 30° Figure 11. This type of motion was originally [6] examined on the grounds that it would prevent interdendritic flow in any single direction and so reduce the probability of channels originating by local melting within the mushy zone. However, in the light of the observations on channel nucleation it now seems more probable that the effect of such movement is to translate the supernatant bulk liquid across the growth front in such a way as to shear or damp out any solute boundary layer perturbations which have or might develop. A certain minimum shear rate seems to be necessary and this is a geometrical function of the mold diameter and probably also of the permeability of the dendritic mesh, although the latter dependence has yet to be demonstrated and will require studies over a significant composition range.

HORIZONTAL HEAT FLOW

As already remarked, this is a more complex situation because the bulk liquid is not quiescent and the gravitational vector is now in the plane of the growth front. Taking the same case, that of d_/dc < d_/dT (negative), liquid rejected at the growth front can raise spontaneously giving a flow pattern such as indicated in Figure 1 (a), and it is probably this type of convection which is primarily responsible for most of the vertical macrosegregation which is to be found in medium to high carbon steel ingots. Undoubtedly, channel flow must contribute something to such macroscopic segregation but it is minon [10]. How the ease of channel nucleation will be affected is not easy to visualize. In as much as the flow will be upwards, both behind and immediately ahead of the growth front, there would seem to be little need for a perturbation at the front nor any driving force to cause local fluid flow out into the bulk liquid, especially as contraction during freezing will draw in the opposite direction. Actually, examination of 'A' segregate patterns in sectioned ingots, Figure 12, or of their formation in the transparent analogue with side chill or of segregation downwards with more dense solute, shows that channels end at the upper or lower surfaces of the columnar zone near the top or bottom of an ingot. Macrosegregation resulting from fluid flows in the bulk liquid, Figure 1(a) or (b), produces higher concentrations at the top or bottom of an ingot, e.g. C in Fe or Pb in Cu, and as this is generally accompanied by a depression in freezing point, the columnar zone is forshortened at one or other end. Therefore, the nucleation mechanisms in this geometrical mode is probably not very different from that in the base chilled arrangement where all the growth front is facing upwards except that interdendritic flow is now more nearly at right angles to, rather than parallel to, the primary dendrite growth axis. This aspect of the problem also means that the permeability of the dendritic mesh to vertical flow is probably reduced, although how relevant this may be to channel formation remains an open question.

Understandably, the effects of mold movements also differ between these two extremes of heat flow direction. At present, the type of movement examined for side chill has involved rotation about only a single axis, Figure 13, which is not quite the same as the precessional movement described for cylindrical molds with base chill, Figure 12. Only the transparent analogue system has been examined, and this simpler bulk liuqid movement does not significantly retard channel formation in such cases. However, it does considerably reduce the extent of macrosegregation in the upper region of the bulk liquid, presumably because of general mixing within the central region of the casting. There is clearly considerable scope for further studies in side chilled arrangements of different shapes and also a need to extend such work to metallic systems, not only in systems with low melting points but in more refractory materials on a scale comparable with actual foundry practice.

DISCUSSION OF PERTURBATION MECHANISM

Referring to the model depicted in Figure 9 for liquid perturbation at a horizontal dendritic growth front, the situation concerns essentially tow liquid layers, the upper and more dense having a decreasing density gradient upwards, determined by the positive temperature gradient, and the lower and less dense having a decreasing density downwards within the dendritic mesh. It is now widely recognized that such density inversion does not necessarily result in spontaneous convective flow patterns and metastable conditions can

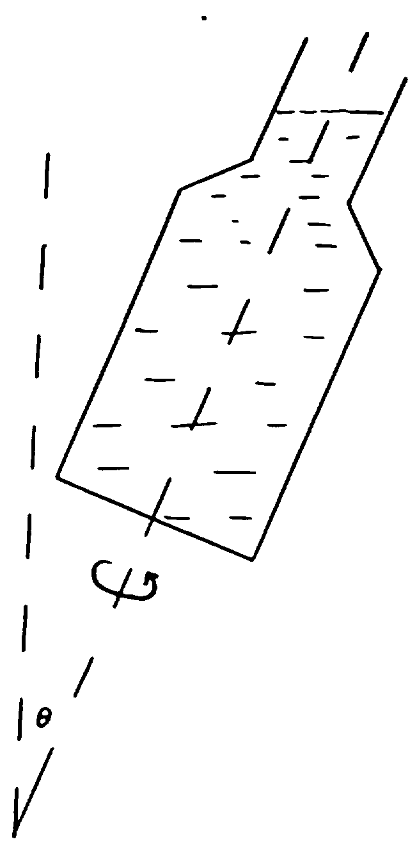


Figure 11.

prevail over wide ranges and dimensions. In metallurgical or materials processing contexts, density inversion can occur at any growth front where solute is rejected with attendant density gradients and it can also occur when two immiscible liquids exist [11]. In a wider context and larger scale it is frequently found in aqueous solutions (e.g. 12) where it has relevance to oceanographic studies [13] and in molten salts, magmas and even stellar interiors [14].

The present case is similar to that of plane front crystal growth upwards with rejection of a less dense solute and positive temperature gradient, but differs in that the growth front is of a permeable semi-solid array in which liquid movement are restricted by viscous drag in fine capillaries of irregular section. Analysis of conditions which lead to perturbations is complicated but has recently been considered in some detail for the plane front problem [15,16] where stabilization by thermal gradients is counteracted by solutal gradients and is described

Figure 12.

as a double diffusive problem, Figure 14 where heat and solutal diffusion are both involved. The resistance to growth of a perturbation arises from liquid viscosity, inertia of the liquid and the adjustment of local temperature at the perturbation to that of the ambient temperature. An important (dimensionless) number which connects these parameters is the Prandtl number, _ = _/$D_{thermal}$ where _ = kinematic viscosity (dynamic viscosity, _, divided by density) and $D_{thermal}$ = thermal diffusivity (thermal conductivity divided by specific heat). For liquid metals _ is small (_ 10^{-2}) while for molten inorganic salts it is larger (_ 10) and for aqueous solutions very large (_ 10^{3}): these relative values physically mean that in metals, temperature can adjust rapidly to local fluctuations of liquid volumes while it cannot easily do so in aqueous solutions - flow in liquid metals is therefore more likely to be streamlined and in the other cases turbulent because locally there develop very steep temperature gradients.

For a perturbation to develop both solute and heat must diffuse simultaneously if it is to grow continuously as density changes from solute concentration and temperature gradients interact. The latter are also connected by Rayleigh numbers (dimensionless), both solutal and thermal, but the ratio of the diffusion coefficients, _ = $D_{Solute}/D_{Thermal}$ is an important number controlling the formation of solute plumes or fingers, such as those which precede channel development. Figure 15 is from a paper by Turner [13] in which the propensity to form solute plumes/fingers is expressed as a thermal:solutal flux ratio, of which a low value corresponds to faster growing perturbation waves or streams; various regimes are then identified on a plot of _ vs. _ and it is shown that liquid metals perturb much more rapidly than aqueous solutions. it is therfore apparent that this particular problem of channel development is just one facet of a general phenomenon.

To pursue the perturbation model further, it has been suggested [7] that the permeability of the two phase, solid + liquid, array behind the growth front Is especially important in allowing a temporary disturbance to develop into a self sustaining plume - precisely because it is permeable to entrainment on all sides; a planar solid front could not as easily sustain such steady state flow because it lacks a path for entrainment between convective fingers. It is also interesting to reconsider some of the aspects of channel development which have been described, in the light of this discussion. Two points are notable. Firstly, channels require some 'incubation' time to develop during which two things occur, (a) the volume of less dense liquid rises towards some critical level above which the buoyancy force becomes considerable, and (b) simultaneously, the temperature gradient in the bulk liquid falls and the resistance to perturbation of the supernatant liquid is steadily reduced; this is why freckle formation in ESR ingots is reduced by high temperature gradients [5]. At some point in time perturbation becomes inevitable. The second point concerns the apparent ease with which channels form in both the aqueous and metallic examples, despite the foregoing conclusion that perturbations of the former should be much more difficult. A possible explanation for this apparent

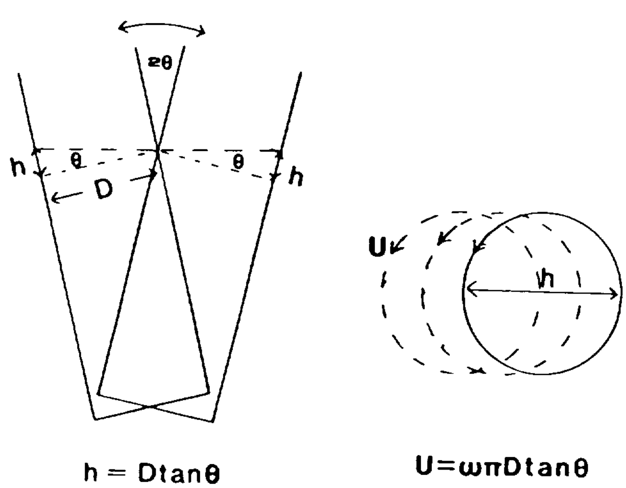


Figure 13.

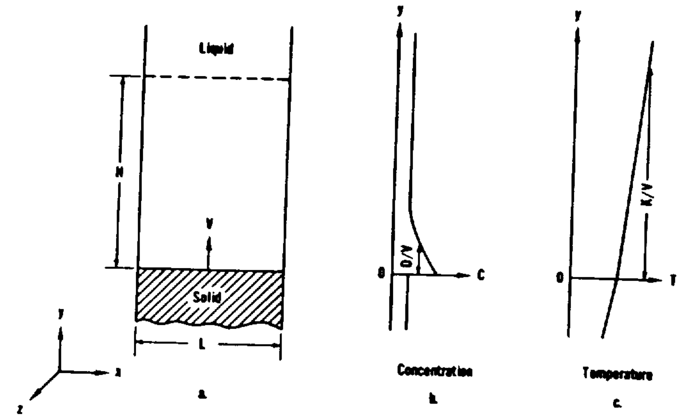


Figure 14.

contradiction is that the aqueous and metallic alloy compositions so far studied, Figure 6, are such that in the former the proportion of liquid in the mushy zone is > 90%, while in the latter only ~10%. The extremely high permeability of composition ranges which can be experimentally studied in the transparent analogue is therefore not comparable with that in the metallic alloy which has so far been examined. There is therefore a pressing need to determine the influence of permeability upon this phenomenon.

SUMMARY AND CONCLUSIONS

1. Segregation channels in the mushy zone of alloy castings develop at the dendritic growth front and not elsewhere behind that front.

2. The channel formation follows behind a perturbation from the less dense layer of interdendritic liquid into the thermally stable (to convection) layer of supernatant bulk liquid. The conditons which favor such perturbations are a larger volume (depth) of the lower density layer and a low temperature gradient in the upper layer.

3. This example of density inversion and the need for a mechanism to start localized convective flow is one of a wider and more general phenomenon which is encountered in oceanographhic contexts, albeit on much larger scales.

4. While channels can be eliminated by choosing alloy systems and compositions which minimize solutal density gradients, they are also expected to disappear with reduced gravity. Bulk liquid movements which translate across the growth front can effectively dampen or shear perturbations and so prevent channel development.

5. There is a need for more studies of arrangements with horizontal heat flow and of the influence of alloy composition and therefore of interdendritic permeability on the case of channel formation.

6. It would be instructive to scale up studies of this type in dimension and temperature to those typical of foundry conditions where the formation channel defects presents a problem.

REFERENCES

1. R. Mehrabian, M. Keane and M. C. Flemings, "Interdendritic Fluid Flow and Macrosegregation; Influence of Gravity", Metall. Trans A, Vol. 1A, pp. 1209-1220 (1970).

2. S. Kou, D. R. Poirier and M. C. Flemings, "Macrosegragation in Rotated Remelted Ingots", Metall. Trans. B, Vol. 9B, pp. 711-719 (1978).

3. R. J. McDonald and J. D. Hunt, "Fluid Motion Through the Partially Solid Regions of a Casting and Its Importance in Understanding 'A' Type Segregation", Trans. Met. Soc. AIME, Vol. 245, pp. 1993-1997 (1969).

4. R. J. McDonald and J. D. Hunt, "Convective Fluid Motion Within the Interdendritic Liquid of a Casting", Metall. Trans. A, Vol. 1, pp. 1777-1778 (1970).

5. S. M. Copley, A. F. Giamei, S. M. Johnson and M. F. Hornbecker, "The Origin of Freckels in Unidirectionally Solidified Ingots", Metall. Trans. A, Vol. 1, pp. 2193-2204 (1970).

6. A. K. Sample and A. Hellawell, "The Effect of Mold Precession on Channel and Macrosegregation in Ammonium Chloride-Water Analog Casting", Metall. Trans. B, Vol. 13B, pp. 495-501 (1982).

7. A. K. Samples and A. Hellawell, "Mechanisms of Formation and Prevention of Channel Segregation During Alloy Solidification", Metall. Trans. A, Vol. 15A, pp. 2163-2173 (1984).

8. K. M. Fisher and J. D. Hunt, "Observations on the Nature and Extent of Gravitational Interdendritic Fluid Flow", Sheffield International Conference on Solidification and Casting, Metals Society, book 193, pp. 325-330 (1977).

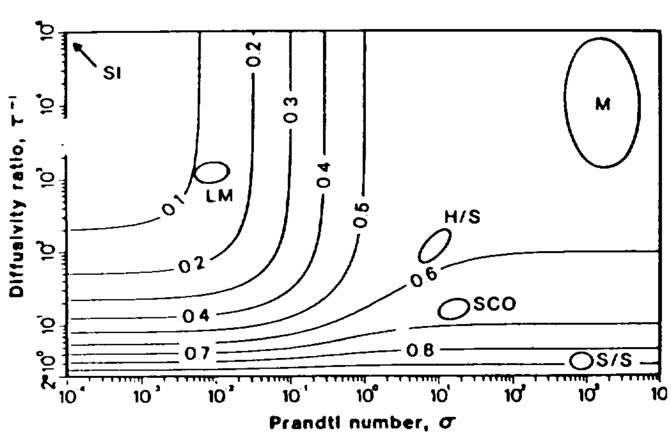


Figure 15.

9. A. K. Sample, "Mechanisms of Formation and Elimination of Channel Segregation During Alloy Solidification", M. S. Thesis, Michigan Technological University (1984).

10. B. E. Watts and P. C. Morgan, "Segregation in 'Wide-End-Up' Ingots", E.C.S.E. Research Project, British Steel Corporation Ref. FR29-14/821 (1982).

11. R. N. Grugel, T. A. Lograsso and A. Hellawell, "Directional Solidification of Alloys in Systems Containing a Liquid Miscibility Gap", Materials Processing in the Reduced Gravity Environemnt of Space, Proceedings of the Materials Research Society. Vol. 9, pp. 553-561 (1982).

12. C. F. Chen, "Double Diffusive Convective Flow", Modeling of Casting and Welding Processes II, Metallurigical Society of AIME, pp. 13-16 (1984).

13. J. S. Turner, "Buoyancy Effects in Fluids", Cambridge University Press, London (1973).

14. J. S. Turner, "Multicomponent Convection", Annual Reviews of Fluid Mechanics, Vol. 17, pp. 11-44 (1985).

15. S. R. Coriell, M. R. Cordes, W. J. Boettinger and R. F. Sekerka, "Convective and Interfacial Instabilities During Undirectional Solidification of a Binary Alloy, J. Crystal Growth, Vol. 49, pp. 13-28 (1980).

16. G. B. McFaddan, R. G. Rehm, S. R. Coriell, W. Chuck and K. A. Morrish, "Thermosolutal Convection During Directional Solidification", Metall. Trans. A, Vol. 15A, pp. 2125-2137 (1984).

17. V. R. Voller, J. J. Moore and N. A. Shah, "Modification of Mathematical Analyses and Related Physical Discriptions Used to Describe Channel Segregation", Metals Technology, Vol. 10, pp. 81-84 (1983).

18. M. R. Bridge, M. P. Stephenson and J. Beech, "Direct Observations on Channel Segregate Formation in Aluminum Alloys", Metals Technology, Vol. 9, pp. 429-433 (1982).

NOTES